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Document Title: Study #202: Protocol for Monitoring the Occurrence and Concentrations of Oryzalin in the San Joaquin River Basin

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I. Introduction

Based on an evaluation of surface water monitoring data and pesticide use practices, oryzalin was identified as one of the pesticide active ingredients that need further characterization of trends and concentrations in surface water (Guo and Spurlock, 2000). Oryzalin was chosen for further study because of:

- its extensive use;
- its high potential for offsite movement to surface water;
- its relatively high aquatic toxicity; and
- a lack of historic monitoring data.

Oryzalin is a selective pre-emergence herbicide used for control of annual grasses and broadleaf weeds in fruit trees, nut trees, vineyards, and ornamentals. It is applied mostly between November and March, coinciding with the rainfall season in the Central Valley, California (Figure 1). The high precipitation can often lead to runoff, causing a potential loss of oryzalin to surface water. In 1993 and 1997, as part of the National Water-Quality Assessment (NAWQA) program, the U.S. Geological Survey (USGS) monitored the presence of oryzalin in surface water in both Sacramento River (SR) and San Joaquin River (SJR) basins (Panshin et al., 1998; Domagalski, et al., 1998). Low concentrations of oryzalin were detected in the SR basin (at <1.51 ppb), but were not in the SJR basin. These results are contrary to expectations based on use data in the Department of Pesticide Regulation's Pesticide Use Report (PUR). Historically the amount of oryzalin applied in the SJR basin was always substantially higher than that in the SR basin (Figure

2). The lack of detections in the SJR basin was probably due to the sparse sampling schedule and/or the higher method detection limit (0.33 ppb for SJR vs. 0.019 ppb for SR) employed in that study (Panshin et al., 1998). Besides these USGS monitoring activities, no other studies have been taken investigating contamination of oryzalin in California surface water. The purpose of this study is to further investigate the occurrence and concentrations of oryzalin in the SJR basin. We will use a more intensive sampling frequency with an improved method detection limit for chemical analysis. The study will be taken during the high use period of oryzalin in the SRJ basin and through the major rainy season so that any contamination, if present, will be more likely to be detected. The surface water quality data collected from this study, however, would probably represent the worst case scenarios and would not reflect baseline concentrations present during the low use period of oryzalin.

II. Objectives

Because of resource limitations, this study will focus only on the SJR basin which is located in the high use area of oryzalin (Figure 2). The objective of this study is to characterize the occurrence and concentration of oryzalin in the SJR basin during its peak use period.

III. Personnel

This project will be conducted by the Environmental Monitoring and Pest Management branch under the general direction of Marshall Lee, Senior Environmental Research Scientist (Supervisor). Other key personnel will include:

Project Leader: Lei Guo
Field Coordinator: Nina Bacey
Laboratory Coordinator: Carissa Ganapathy
Senior Scientist: Frank Spurlock
Agency and Public Contact: Pat Dunn

Questions regarding this monitoring study should be directed to Pat Dunn at (916) 445-3097 or pdunn@cdpr.ca.gov.

IV. Study Plan

Due to the limitation in resources, the sampling sites and schedule for oryzalin monitoring will be identical to those for the on-going dormant spray runoff study (Study #200) so that sampling activities for the two studies can be completely combined and cost minimized. The use period for oryzalin is primarily between October and March, which coincides substantially with the major dormant spray period (Figure 1). The sampling for Study #200 (hence this study) will start in January of 2001, and continue until the middle of March of 2001. This study period thus will cover the peak use period of oryzalin in the San Joaquin Valley.

Based on the existing plan of Study #200, surface water samples will be collected at two monitoring sites, chosen to represent water quality conditions associated with two distinguishing characteristics of the SJR basin (Figure 3). The first site is located at the main stem of the SJR near Vernalis. This site is considered to be an integrator site for the entire SJR basin, as it receives flows from all subbasins, and therefore reflects water quality conditions as affected as a whole by the land use, hydrology, pesticide application, and other factors in the entire basin (Panshin et al., 1998). The second site is located at Orestimba Creek, a western tributary to the SJR in the midst of agricultural lands. Water at this site is comprised of mainly drainage and irrigation returns from the agricultural lands, and thus its quality would be very sensitive to agricultural runoff or any other transport pathways leading to contamination. Both of these sites are facilitated with USGS flow gauges, and discharge records will be available for late estimation of total mass loading if so desired.

The sampling of surface water at Vernalis site will be conducted three times every week, on Monday, Wednesday, and Friday, and at Orestimba Creek twice on Monday and

Wednesday during the monitoring period (January to March, 2001), which will result in a total of 61 water samples, including 55 field water samples and 6 spikes. Ideally, at least one sampling event should be taken prior to the major application of oryzalin in the SJR basin area to provide baseline concentration information in surface water. However, the restricted resource and laboratory capability available to this project are such that any deviation from the established sampling schedule would be unfeasible.

V. Sampling Method

Surface water samples will be collected using a depth-integrated sampler (D-77) with a 3-liter Teflon® bottle and nozzle. The water will be poured directly into 2 1-L amber glass bottles and sealed with Teflon-lined lids. The bottles will then be stored immediately on wet ice until delivered to the Laboratory for chemical analysis. During each sampling event, dissolved oxygen, pH, specific conductance and water temperature will be measured *in situ* at each site.

VI. Chemical Analysis

Water samples will be analyzed by the California Department of Food and Agriculture (CDFA) laboratory for oryzalin, using the modified ground water method #50.5. This method had a detection limit of 0.05 ppb. However, due to the presence of suspended solids normally in the surface water, the final detection limit for surface water samples is expected to be higher. The modifications to be made to the analytical procedure will be determined and tested by the CDFA laboratory. The potential changes may include filtering of surface water samples, increases in the extracted volume and/or increases in final injection volume. The target goal of the modified procedure is to attain a method detection limit which is comparable to that for ground water samples (<0.1 ppb).

VII. Data Analysis

The monitoring data will be analyzed in several possible ways depending mainly on the frequency of detection. If there are only a few detections (for example <10%), indicating pulse-type (i.e., noncontinuous) inputs, the data analyses will be focused on extraordinary events, such as the occurrence of heavy storms, the high application rate of the pesticide in a particular area, or a combination of both, which are usually causes for noncontinuous sources. Data of breakpoint rainfall events and pesticide uses will be obtained from the Statewide Integrated Pesticide Management Project, University of California, Davis, and our own department, respectively, to analyze the potential relationship between storm/application event characteristics and surface water quality.

In the case that the detection frequency is sufficiently high, estimation of mass loading will be attempted. This will be accomplished by assuming certain relationship between the concentration and flow characteristics. Reinelt and Grimvall (1992) presented four different methods for estimation of nonpoint source loadings in watersheds: (i) stepwise constant concentration; (ii) linear interpolation of concentration; (iii) linear relationship between flow and concentration; and (iv) linear relationship between log(load) and log(flow). These methods will be used to calculate oryzalin loss fractions, and compare losses over time and among events. Finally, a more thorough and comprehensive approach for watershed data analysis may be taken by employing modeling. A watershed model may be identified to evaluate the runoff and transport behavior of oryzalin in the SJR basin. Modeling exercises can also provide insights into the functional relationships among various watershed parameters and processes.

VIII. Time Table

Field Sampling: January 2001 through March 2001
Chemical Analysis: December 2001 to April 2001
Preliminary Report: August 2001
Final Report: December 2001

IX. References

Domagalski, J. L., D.L. Knifong, D.E. MacCoy, P.D. Dileanis, B.J. Dawson, and M.S. Majewski. 1998. Water quality assessment of the Sacramento River Basin, California – Environmental setting and study design. U.S. Geological Survey, Water-Resources Investigations Report 97-4254, 31 p.

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Panshin, S.Y., N.M. Dubrovsky, J.M. Groberg, and J.L. Domagalski. 1998. Occurrence and distribution of dissolved pesticides in the San Joaquin River Basin, California. U.S. Geological Survey, Water-Resources Investigations Report 98-4032, 88 p.

Reinelt, L.E. and A. Grimvall. 1992. Estimation of nonpoint source loadings with data obtained from limited sampling programs. *Environmental Monitoring and Assessment* 21:173-192.

Figure 1. Oryzalin Use Pattern by Month
(1990-1998)

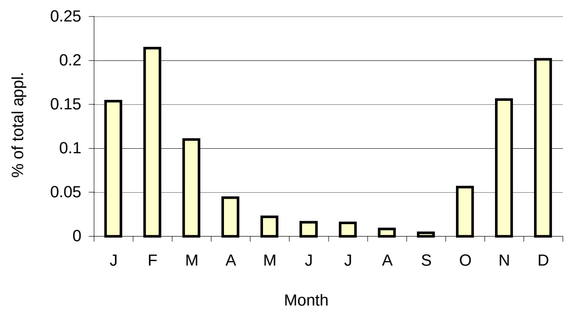
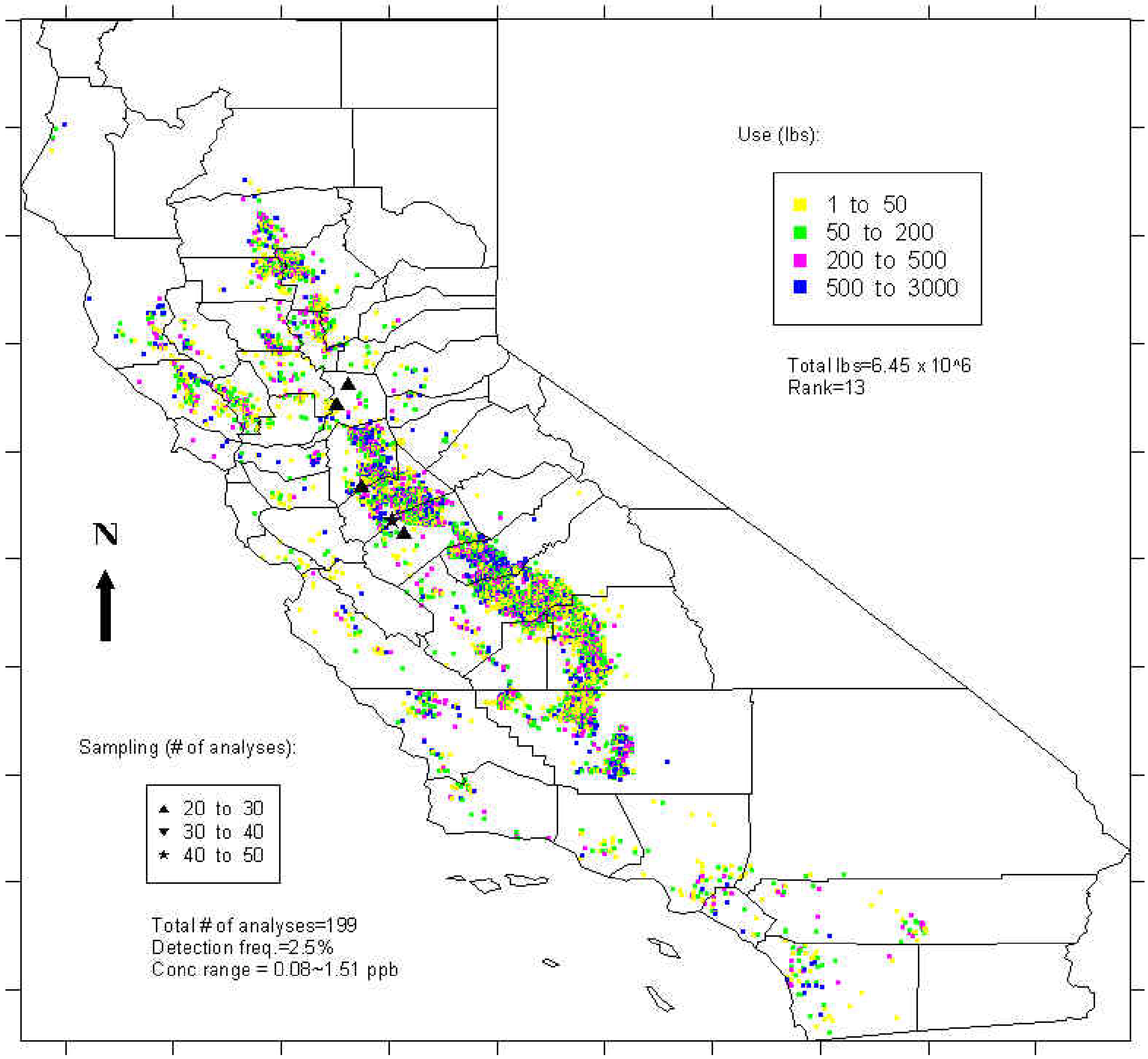


Figure 2. Oryzalin use (1990-1998) and surface water sampling (1990-2000) locations in CA.
Source: PRD and SURF, Department of Pesticide Regulation



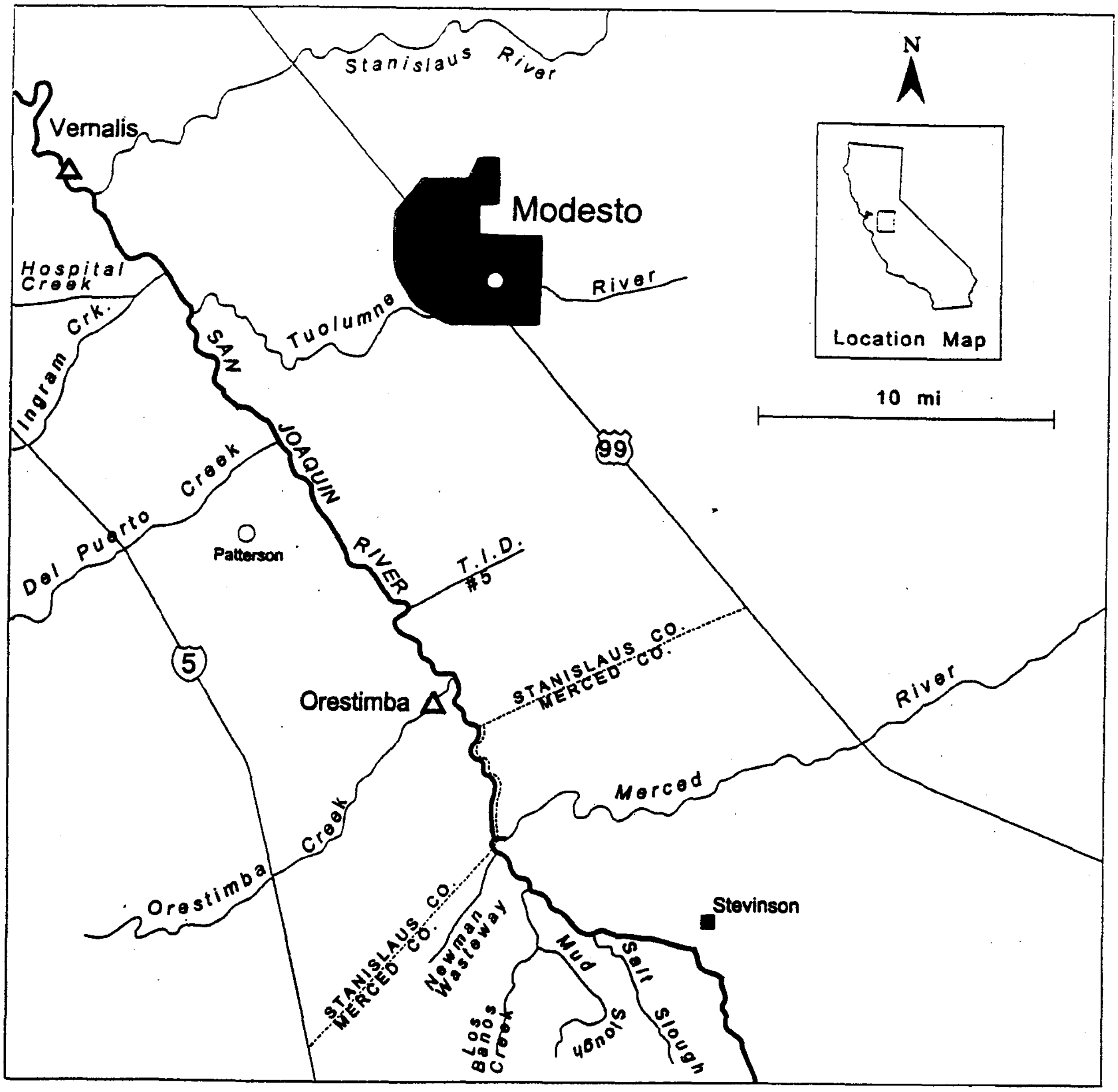


Figure 3. Sampling Locations (△) for Oryzalin Monitoring in the San Joaquin River Basin.